United States Patent

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Continuation-in-part of application Ser. No. 682,546, Nov. 13, 1967, now Patent No. 3,513,097, which is a continuation-in-part of application Ser. No. 516,077, Dec. 23, 1965, now abandoned.

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[54] **POLYESTER FUNCTIONAL FLUID COMPOSITIONS**
8 Claims, No Drawings

[52] **U.S. Cl.** **252/79,** 252/56, 252/389, 252/76
[51] **Int. Cl.** **C09k 3/00,** C10m 3/20, C23f 11/08
[50] **Field of Search** 252/73–79, 56, 388, 389

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ABSTRACT: Compositions comprising a synthetic ester hydraulic fluid and a small amount of water exhibit the ability and control damage to mechanical members in contact with said compositions. The compositions have many uses, among which are their use as hydraulic fluids.

POLYESTER FUNCTIONAL FLUID COMPOSITIONS

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This application is a continuation-in-part of application Ser. No. 682,546, filed Nov. 13, 1967 now U.S. Pat. No. 3,513,097, which is a continuation-in-part of application Ser. No. 516,077, filed Dec. 23, 1965, now abandoned.

This invention relates to functional fluid compositions having an ability to inhibit and control damage to mechanical members in contact with said fluid compositions, to functional fluid compositions which exhibit an improved tendency to resist fluid degradation and more particularly to compositions comprising certain functional fluids and an additive amount, sufficient to inhibit and control damage, of water.

Many different types of materials are utilized as functional fluids and functional fluids are used in many different types of applications. Thus, such fluids have been used as electronic coolants, diffusion pump fluids, lubricants, damping fluids, bases for greases, power transmission and hydraulic fluids, heat transfer fluids, heat pump fluids, refrigeration equipment fluids and as filter mediums for air-conditioning systems. In many of these uses there have been reports of damage to the fluid during use and to mechanical members, especially metallic members, in contact with the fluid as evidenced by a loss of weight of such members. Thus, damage has been reported in aircraft hydraulic systems, jet turbine control systems, and steam turbine control systems. Damage has also been observed on such materials as glass, Teflon Mylar, Plexiglass and other members constructed from materials other than metals.

One particularly undesirable condition which exists during the use of a functional fluid and which can cause damage is cavitation, which can be described as a phenomenon which results in the formation and subsequent violent collapse of vapor-filled bubbles in a fluid subjected to requisite pressure changes. Bubbles can be formed when the fluid pressure is at or below its bubble point pressure and when fluid temperature peaks above fluid bubble point temperature; above the bubble point pressure, the bubbles collapse. Pressure changes sufficient to cause cavitation can occur in several ways; for example, a fluid flowing through a restriction, such as a partially closed valve, can encounter at the point of highest velocity a pressure far lower than both the bubble point and the valve outlet pressures thus resulting in bubble formation. As these bubbles reach a point of high pressure, for example on the discharge side of the valve, a violent collapse of the bubbles occurs thereby producing shock waves which can be severe enough to damage the fluid and mechanical members in contact with the fluid. As another example, cavitation conditions can occur when a surface is moved through or vibrated in a relatively stagnant liquid.

While there are many undesirable results caused by damage, one important aspect of the problem of damage is the effect on hydraulic systems and fluids experiencing such damage. For example, the structural mechanical parts in a hydraulic system, such as pumps and valves, exhibit a marked decrease in strength, and the geometry of the parts is altered. Such changes in the case of valves can cause faulty operations, excessive leakage or even hazardous conditions. As a result, damage necessitates premature overhaul of mechanical parts which is both costly and time consuming. In addition, as damage occurs the metal from metallic mechanical parts in contact with the functional fluid contaminates the fluids requiring premature draining of the fluids from the system, filter clogging and excessive filter replacement, and can cause a change in physical and chemical properties of the fluids. Also, metal contaminants can reduce the oxidative stability of a fluid thereby adversely affecting fluid performance. In addition to any effects resulting from contamination by metal (or other) contaminant, such damage to the fluid can manifest itself in numerous ways, among which are (a) viscosity change, (b) increase in acid number, (c) formation of insoluble materials, (d) increased chemical reactivity and (e) discoloration.

It is, therefore, an object of this invention to provide functional fluid compositions having an ability to inhibit and control damage.

Further objects will be apparent from the following description of the invention.

It has now been found that damage, herein defined to include damage to a functional fluid and to mechanical members in contact with said fluid, can be effectively controlled and inhibited in the functional fluid systems described by the incorporation of damage inhibiting amounts of water into the functional fluid. It is an important part of this invention that the incorporation of water in functional fluids produces a functional fluid composition having the ability to inhibit damage without completely affecting adversely other essential properties of such fluids such as viscosity, oxidative and thermal stability, corrosion resistance in the presence of metal parts and the lubricating qualities of the functional fluid.

The concentration of water in a functional fluid is adjusted in terms of the particular system and the functional fluid which is utilized in this system to provide functional fluid compositions of this invention which contain and additive amount of water sufficient to inhibit and control damage. Thus, for the functional fluid compositions of this invention comprised of synthetic ester fluids, the concentration of water in the composition can vary from 0.20 volume percent to about 5 volume percent, the particular concentration being that amount which will effectively inhibit and control damage. The preferred additive concentration range in the functional fluid compositions of this invention is from 0.30 volume percent to about 2 volume percent of water, and even more preferably from 0.35 volume percent to about 1.5 volume percent of water. The compositions of this invention are prepared by incorporating a damage inhibiting amount of water into a synthetic ester fluid, the base stock of the functional fluid. Thus, the process for preparing a functional fluid having the ability to inhibit and control damage to mechanical members in contact with the functional fluid is accomplished by adding water to a functional fluid to obtain a concentration of water in the functional fluid of from 0.20 volume percent to about 5 volume percent. In carrying out the process, water is added to the composition with sufficient agitation to incorporate additive amounts of water.

The functional fluids, to which water is added to provide the functional fluid compositions of this invention, include functional fluids comprising a major amount of a base stock which is a synthetic ester fluid, or a blend of a synthetic ester fluid with an amide of an acid of phosphorus and/or esters of an acid of phosphorus and/or aromatic ether compounds and/or with halogenated blending agents, representative of which are halodiphenyl ethers, halobenzenes, halonaphthalenes, haloalkylated benezenes, perhalodienes and perhalocyclicdienes.

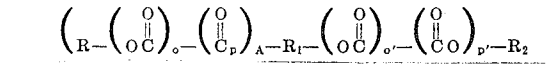
Whereas the above base stock can be utilized to prepare functional fluid compositions of this invention when utilized in major amounts, it is preferred to use such base stock at a concentration of at least about 60 weight percent and even more preferably at concentrations of 65, 75, 85 and 95 weight percent or the above concentrations at a corresponding volume percent.

In general, when the base stock that is utilized to prepare a functional fluid composition of this invention is to be utilized in, for example, hydraulic systems which require the utmost of purity, such as certain types of high-response aircraft hydraulic systems, it is preferred to have a base stock which has an acid number of 0.50 or less, even more preferably 0.35 or less and still more preferably 0.15 or less. "Acid number" is herein defined as the number of milligrams of potassium hydroxide required to neutralize 1 gram of sample. Thus, for example, synthetic ester fluids are utilized as a base stock to prepare functional fluid compositions of this invention, it is preferred that such base stocks have acid numbers within the limits as set forth above when such base stocks are to be utilized in high-response aircraft hydraulic systems. Thus, the compositions of this invention when incorporated initially in aircraft

hydraulic systems should be within the acid number limits as set forth above.

The following base stocks are only illustrative of typical base stocks that can be utilized in preparing the functional fluid compositions of this invention and the instant invention can be practiced utilizing various modifications of the base stocks which are set forth below.

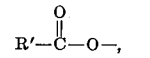
The synthetic ester fluids which are suitable as base stocks for the composition of this invention are di- and tricarboxylic acid esters represented by the structure



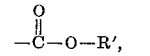
wherein o, o', p and p' each are whole numbers having the value of 0 to 1 provided that the sum of each of $o+p$ and $o'+p'$ is 1; A is a whole number having a value of 1 to 2; R and R_2 are each independently selected from alkyl, alkoxyalkyl, cycloalkyl, alkyl cycloalkyl, aralkyl, alkaryl, and members of the above group further substituted by halogen and R_1 is selected from alkylene, alkenylene, phenylene and members of the above group further substituted by carboxy, carboalkoxy or acyloxy.

Typical examples of the alkyl radicals which R and R_2 represent are as follows: methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl, tert-butyl, n-amyl, isoamyl, 2-methylbutyl, 2,2-dimethyl propyl, 1-methyl butyl, diethyl methyl, 1,2-dimethyl propyl, tert-amyl, n-hexyl, 1-methylamyl, 1-ethyl butyl, 1,2,2-trimethyl propyl, 3,3-dimethyl butyl, 1,1,2-trimethyl propyl, 2-methyl amyl, 1,1-dimethyl butyl, 1-ethyl 2-methyl propyl, 1,3-dimethyl butyl, isohexyl, 3-methylamyl, 1,2-dimethyl butyl, 1-methyl 1-ethyl propyl, 2-ethyl butyl, n-heptyl, 1,1,2,3-tetramethyl propyl, 1,2-dimethyl 1-ethyl propyl, 1,1,2-trimethyl butyl, 1-isopropyl 2-methyl propyl, 1-methyl 2-ethyl butyl, 1,1-diethyl propyl, 2-methyl hexyl, 1,1-dimethyl amyl, 1-isopropyl butyl, 1-ethyl 3-methyl butyl, 1,4-dimethyl amyl, isoheptyl, 1-methyl 1-ethyl butyl, 1-ethyl 2-methyl butyl, 1-methyl hexyl, 1-propyl butyl, n-octyl, 1-methyl heptyl, 1,1-diethyl 2-methyl propyl, 1,1,3,3-tetramethyl butyl, 1,1-diethyl butyl, 1,1-dimethyl hexyl, 1-methyl 1-ethyl amyl, 1-methyl 1-propyl butyl, 2-ethyl hexyl, 6-methyl heptyl (iso-octyl), n-nonyl, 1-methyl octyl, 1-ethyl heptyl,1,1-dimethyl heptyl, 1-ethyl 1-propyl butyl, 1,1-diethyl 3-methyl butyl, diisobutyl methyl, 3,5,5-trimethyl hexyl, 3,5-dimethyl heptyl, n-decyl, 1-propyl heptyl, 1,1-diethyl hexyl, 1,1-dipropyl butyl, 2-isopropyl 5-methyl hexyl, decyl radicals, e.g. n-decyl dodecyl radicals, e.g. lauryl, tetradecyl radicals, e.g. myristyl, hexadecyl radicals, e.g. cetyl; and octacecyl. Typical examples of aralkyl radicals, aryl for the purpose of any aryl-containing radical is herein defined to include mono-, di- and polynuclear hydrocarbons, such as phenyl napthyl and anthryl, e.g. aryl and alkylaryl-substituted alkyl radicals, are benzyl methylbenzyl, caprylbenzyl, diisobutylbenzyl, phenylethyl, phenylpropyl, phenyloctadecyl; xenyl- and alkylxenyl-substituted alkyl radicals, e.g. xenylmethyl, caprylxenylmethyl, xenylethyl, diisobutylxenylmethyl; naphthyl- and alkylnapthyl-substituted alkyl radicals, e.g. naphthylmethyl, tert-amylnapthylmethyl, naphthylethyl and octylnaphthylethyl. Typical examples of oxygen-containing alkyl radicals, e.g. alkoxy-substituted alkyl radicals, are propoxyethyl radicals, e.g. n-propoxyethyl, isopropoxyethyl; butoxyethyl radicals, e.g. n-butyoxyethyl, isobutoxyethyl, tert-butoxyethyl; octoxethyl radicals, e.g. n-octoxyethyl, diisobutoxyethyl; dibutoxypropyl radicals, e.g. 2,3-di-n-butoxypropyl, 3,3-diisobutoxypropyl; dioctoxypropyl and 2,3-bis(diisobutoxy)propyl. Typical examples of aroxy-substituted alkyl radicals are, for example, phenoxy- and alkylphenoxy-substituted alkyl radicals, e.g. phenoxymethyl, phenoxyethyl, cetylphenoxyethyl, and caprylphenoxyethyl. Typical examples of aryl alkoxyaryl, aroxyaryl and halo and alkyl derivatives thereof are phenyl, cresyl, xylyl, mesityl, ehtylphenyl, diethylphenyl, isopropylphenyl, n-propyl-phenyl, tert-butylphenyl, di-tert-butylphenyl, isobutylphenyl, n-butylphenyl, tert-amylphenyl, cuclohexylphenyl, methylcyclo-hexylphenyl, caprylphenyl, diisobuthylphenyl, laurylphenyl, cetylphenyl, paraffin wax-substituted phenyl, monochlorophenyl, polychlorophenyl e.g. dichlodrophenyl, trichlorophenyl, lauroxyphenyl, xenyl, mono- and polychloroxenyl, caprylxenyl, phenoxy-phenyl, thiophenoxyphenyl, diisobutylphenoxyphenyl, naphthyl, mono- and polychloronaphthyl, cetylnaphthyl, methylmonochlorophenyl radicals, methylpolychlorophenyl radicals, e.g. methyldichlorophenyl radicals and methyltrichlorophenyl radicals.

Typical examples of alkylene and alkenylene which R_1 represents are methylene, ethylene propylene, tetramethylene, pentamethylene, octamethylene, decamethylene, 2-propenylene and alkenylene and alkylene radicals having from 1 to 16 carbon atoms. Typical examples of cycloalkyl and alkyl cycloalkyl radicals which R and R_2 represent are cyclopentyl, alkylated cyclopentyl, cyclohexyl and alkylated cyclohexyl radicals, e.g. mono- and polymethylcyclopentyl radicals, mono- and polymethylcyclohexyl radicals, mono- and polyethylcyclohexyl radicals, mono- and polyisopropylcyclohexyl radicals, mono- and poly-tert-amylcyclohexyl radicals, n-octylcyclohexyl radicals, diisobutylcyclohexyl (i.e., "tert-octyl"-cyclohexyl) radicals, nonylcyclohexyl radicals, diisoamylcyclohexyl radicals laurycyclohexyl radicals and cetylcyclohexyl radicals. Typical examples of acyloxy,



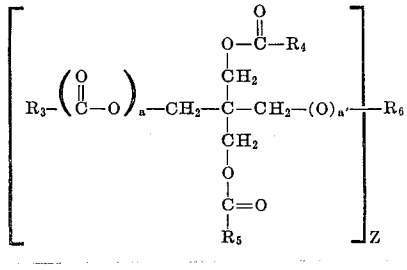
and carboalkoxy,



are those radicals wherein R' in the acyloxy and carboalkoxy radicals is alkyl having from 1 to 18 carbons atoms. Examples of these alkyl groups are illustrated above. With respect to the di- and tricarboxylic acids, it is preferred that R and R_2 be alkyl having from about 2 to about 18 carbon atoms, more preferably from about 4 to about 14 carbon atoms and R_1 be alkylene having from about 2 to about 12 carbon atoms, more preferably from about 4 to about 10 carbon atoms.

Typical examples of synthetic ester fluids which di- and tricarboxylic acid esters are di(2-ethylhexyl) azelate, di(2-ethylhexyl) sebacate, diisooctyl sebacate, 2-ethylhexyl 3:5:5 trimethylhexyl sebacate, diisooctyl azelate, di(3:5:5 trimethylhexyl) sebacate, di(1-methyl-4-ethyloctyl) sebate diisodecyl azelate, diisotridecyl azelate, di(1-methyl-4-ethyl-octyl) glutarate, di(2-ethylhexyl) adipate, di(3-methylbutyl) azelate, di(3:5:5 trimethylhexyl) azelate, di(2-ethylhexyl) adipate, di(C_{10}oxo) adipate, bis(diethylene glycol monobutyl ether) adipate, di(isooctyl/isodecyl) adipate, diisotridecyl adipate, triethylene glycol di(2-ethylhexanoate), hexanediol 1,6-di(2-ethylhexanoate) and dipropylene glycol dipelargonate. Additional examples are mixtures of esters made from an aliphatic dibasic acid and a technical mixture of alcohols such as a mixture of alcohols obtained by the oxo process.

Typical examples of synthetic ester fluids which are polyesters and which are suitable as base stocks in the compositions of this invention are those polyesters represented by the structure



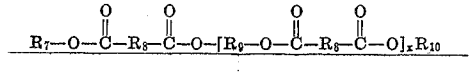
wherein R_3 is selected from the group consisting of hydrogen and alkyl, R_4 and R_5 are each selected from the group consisting of alkyl, alkoxyalkyl, cycloalkyl, alkyl cycloalkyl, aralkyl, aryl, alkylaryl and members of the above group further substituted with halogen, a is a whole number having a value of 0 to 1, a' is a whole number having a value of 0 to 1, Z is a whole number having a value of 1 to 4 and when Z is 1 a' is 0 and R_6 is acyloxy and when Z is 2 to 4 a' is 1 and R_6 is acyl. Typical examples of alkyl, alkoxyalkyl, aralkyl, cycloalkyl, alkyl cycloalkyl, aryl, alkaryl, members of the above group further substituted with halogen, and acyloxy are those illustrated above. With respect to the above polyesters, it is preferred that R_3, R_4 and R_5 be alkyl having from about 2 to 18 carbon atoms, more preferably from about 4 to about 10 carbon atoms and R_6 be acyloxy or acyl having from about 3 to about 12 carbon atoms, more preferably from about 4 to about 10 carbon atoms.

Typical examples of polyester compounds can be prepared by the reaction of an acid compound with a polyhydroxy compound which polyhydroxy compound can be trimethylolpropane, trimethylolethane, pentaerythritol, dipentaerythritol, tripentaerythritol and tetrapentaerythritol.

The acids which may be utilized are, for example, aliphatic monocarboxylic acids, alicyclic monocarboxylic acids, aromatic monocarboxylic acids and heterocyclic monocarboxylic acids, such as propionic, butyric, isobutyric, n-valeric, caproic, n-heptylic, caprilic, 2-ethylhexanoic, 2,2-dimethyl-heptanoic and pelargonic. Typical examples of esters of this type are trimethylolpropane, tri-n-pelargonate, trimethylolpropane tricaprylate, trimethylolpropane tricaprylate, the trimethylolpropane triester of mixed octanoates, pentaerythrityl tetrabutyrate, pentaerythrityl tetravalerate, pentacrythrityl tetracaproate, pentaerythrityl dibutyrate dicarproate, pentaerythrityl butyrate caproate divalerate, pentaerythrityl butyrate trivalerate, pentaerythrityl butyrate tricaproate, pentaerythrityl tributyrate caproate. Suitable dipentaerythrityl esters include dipentaerythrityl hexavalerate, dipentaerythrityl hexacaproate, dipentaerythrityl hexaheptoate, dipentaerythrityl hexacaprylate, dipentaerythrityl tributyrate tricaproate, dipentaerythrityl trivalerate trinonylate, dipentaerythrityl mixed hexaesters of $C_{4\text{-}10}$ fatty acids.

Other examples of esters which are also suitable as base stocks are hydrocarbon monoesters containing one ester group, typical examples of which are isoocytl stearate and 2-ethylhexyl octoate.

Complex esters which are suitable as base stocks in the compositions of this invention are represented by the structure



wherein R_7 and R_{10} are each selected from the group consisting of hydrogen, alkyl, alkoxyalkyl, aralkyl, aryl, alkylaryl, cycloalkyl, alkyl cycloalkyl, R_8 and R_9 are each selected from the group consisting of alkylene, alkenylene and members of the above group further substituted by acyloxy and hydroxyl, x is a whole number having a value of 1 to about 80 or more.

Typical examples of alkyl, alkoxyalkyl, aralkyl, aryl, alkaryl, cycloalkyl, alkyl cycloalkyl, alkylene, alkenylene and acyloxy are illustrated above. With respect to the complex esters, it is preferred that R_7 and R_{10} be alkyl having from about 3 to about 12 carbon atoms, more preferably from about 4 to about 10 carbon atoms and that R_8 and R_9 be alkylene or acyloxy substituted alkylene wherein the alkylene portion contains from about 2 to about 12 carbon atoms, more preferably from about 4 to about 8 carbon atoms and the acyloxy substituent contains from about 2 to about 12 carbon atoms.

Typical examples of complex esters can be obtained by esterifying dicarboxylic acids with a mixture of monohydric alcohol and a glycol to give complex esters. Complex esters which can be employed can be prepared by esterifying a dicarboxylic acid (1 mole) with a glycol (2 moles) and a monocarboxylic acid (2 moles) or with 1 mole each of a glycol, a dicarboxylic acid and a monohydric alcohol or with 2 moles each of a monohydroxy monocarboxylic acid and a monohydric alcohol. Still other complex esters may be prepared by esterifying a glycol (1 mole) with a monohydroxy monocarboxylic acid (2 moles) and a monocarboxylic acid (2 moles).

Other complex esters which are suitable as base stocks are prepared by polymerizing a dihydroxy compound with a dicarboxylic acid and reacting the terminal hydroxy and acid radical with a mixture of monocarboxylic acid and a monohydric alcohol. Specific examples of polymers which may be utilized as additives within the scope of this invention are polymers prepared by the polymerization of adipic acid and 1,2-propane diol in the presence of minor amount of short-chain monocarboxylic acids and a monohydric alcohol to give molecular weights of the polymers thereby produced of from about 700 to about 40,000 or higher.

The mono- , di- and polyhydric alcohols, and the monocarboxylic acids employed in the preparation of the complex esters can also contain ether oxygen linkages.

Specific examples of suitable complex esters are esters prepared from methylene glycol (1 mole), adipic acid (2 moles) and 2-ethylhexanol (2 moles); esters prepared from tetraethylene glycol (1 mole), sebacic acid (2 moles), and 2-ethylhexanol (2 moles); esters prepared from 2ethyl-1-1,3-hexanediol (1 mole), sebacic acid (2 moles) and 2-ethylhexanol (2 moles); esters prepared from diethylene glycol (1 mole), adipic acid (2 moles) and n-butanol (2 moles); esters prepared from polyglycol 200 (1 mole), sebacic acid (2 moles) and ethylene glycol mono(2-ethylbutyl) ether (2 moles); esters prepared from sebacic acid (1 mole), tetraethylene glycol (2 moles) and caproic acid (2 moles); esters prepared from triethylene glycol (1 mole), adipic acid (1 mole), n-caproic acid (1 mole) and 2ethylhexanol (1 mole); esters prepared from sebacic acid (1 mole), lactic acid (2 moles) and n-butanol (2 moles); esters prepared from tetraethylene glycol (1 mole), lactic acid (2 moles) and butyric acid (2 moles); complex esters prepared from neopentyl glycol (2 moles), dicarboxylic acids (1 moles) and monocarboxylic acids (2 moles) and complex esters prepared from neopentyl glycol (1 mole) dicarboxylic acids (2 moles) and monohydric neoalcohols, e.g. 2,2,4-trimethylpentanol (2 moles).

It is contemplated within the scope of this invention that the aforedescribed radicals such as alkyl, aralkyl, alkoxyalkyl aroxyalkyl, aryl, aroxyaryl, alkoxyaryl and alkaryl can have all or part of the hydrogen replaced with halogen such as fluorine, chlorine or bromine.

The invention can be better appreciated by the following nonlimiting examples. In examples 1 and 2, as given in Table I, damage tests were run using mild steel specimens in about 750 to about 1,000 cc. of fluid at a fluid temperature of about 137° F. The metal specimen was vibrated in the fluid at 15 kilocycles with an 0.0002-inch amplitude for a period of 4 hours. In examples 3 through 21 a nickel specimen was immersed in the fluid and a 20 kilocycle vibration induced adjacent to the specimen. The temperature of the fluid was 85° C. and the test duration was 45 minutes.

In example 2, a mineral oil, herein designated Fluid A, was utilized as the test fluid and had the following specification.

Property	Value
Viscosity in centistokes at 54.4° C. (130° F.) (min.)	10.0
Viscosity in centistokes at −40° C. (−40° F.) (max.)	500
Viscosity in centistokes at −54° C. (−65° F.) (max.)	3,000
Pour Point (max.)	−59.4° C. (−75.0° F.)
Flash Point (min.)	93.3° C. (200.0° F.)
Acid or bath No. (max.)	0.20

Each base stock is listed as one separate example, whereas the runs indicate separate runs of that fluid at the various concentrations of water that are so indicated in table I. Relative weight loss is defined to mean the total weight loss of the metal specimen when tested in a fluid containing the additive present divided by the weight loss of the metal specimen when the neat fluid is tested without any additive present, times 100. The volume of water that was added had a specific gravity of 1 at 24° C. The volume percent of water added was determined by dividing table volume of water added by the total volume of the final fluid composition times 100. The weight percent of water in the fluid composition is obtained by dividing the volume of water added by the product obtained by multiplying a volume of the final fluid composition times the density of the final fluid composition, times 100. In general, it has been found that the weight percent of water in the fluid composition at these low concentrations does not vary significantly from the volume percent in water in the fluid composition.

TABLE I

Ex. No.	Fluid compositions	Run	Volume percent water in fluid	Relative weight loss
1	87.5% dibutylphenyl phosphate, 11% Acryloid VI improver, 1% epoxidized soybean oil, .50% bis(1,2-phenylmercapto) ethane.	1	0.50	71
		2	0.75	40
		3	1.25	17
		4	2.25	10
2	Fluid A	1	0.50	70.5
3	4.2% Acryloid VI improver, 47.8% 2-ethylhexyldiphenyl phosphate, 47.8% isooctyldiphenyl phosphate, 10 p.p.m. silicone.	1	0.39	47
		2	0.64	29
		3	1.14	23
4	Dibutylphenyl phosphate	1	0.71	80
		2	1.21	62
		3	2.21	36
5	Tributyl phosphate	1	0.69	84
		2	1.19	49
		3	2.19	32
		4	5.19	4
6	Tricresyl phosphate	1	0.5	47
7	2:1 tributyl phosphate-tricresyl phosphate.	1	1.0	71
8	1:1 tributyl phosphate-tricresyl phosphate.	1	1.0	81
9	Tri(2-butoxyethyl) phosphate	1	1.0	50
10	Dioctyl sebacate	1	0.29	59
11	Pentaerythritol tetravalerate	1	0.45	44
12	70% tributyl phosphate, 22.5% tricresyl phosphate, 7.5% 2-ethylhexyl sebacate.	1	1.0	68
13	68% tributyl phosphate, 20% tricresyl phosphate, 7.5% 2-ethylhexyl sebacate, 4.5% Acryloid VI improver.	1	1.06	40
14	2-ethylhexyldiphenyl phosphate	1	1.05	18
15	Isooctyldiphenyl phosphate	1	1.04	16
16	Chlorinated biphenyl having an approximate chlorine content of 32% by weight.	1	0.25	61
17	Tetra-2-ethylhexyl silicate	1	0.27	68
18	5-ring polyphenyl ether blend, 65% m-bis(m-phenoxyphenoxy) benzene, 33% m-(m-phenoxyphenoxy)phenyl-p-phenoxyphenyl ether.	1	0.30	68
19	49.9% m-bisthiophenoxybenzene, 49.9% a mixture of 4-ring thioethers and mixed thiooxyethers.	1	0.28	15
20	N-methyl-N-butyl-N'-methyl-N'-butyl-p-phosphorodiamidate.	1	1.02	54
21	75% 3-chloro-4'-bromodiphenyl ether, 25% 3-chlorodiphenyl ether.	1	0.55	61

The test method as employed to determined relative damage has been found to correlate quite well to actual test runs on simulated hydraulic system test stands, such as the Fairey Test Stand, and has correlated quite well with the hydraulic system of commercial aircraft where damage levels have been determined. Functional fluid compositions of this invention with additive water sufficient to inhibit and control damage have been evaluated in actual hydraulic systems in test stands and commercial aircraft and have been found to effectively inhibit damage and are far superior to the neat fluids without additive amounts of water.

It is believed that the cause of cavitation damage in aircraft hydraulic systems is by a pressure excursion process whereby the fluid pressure dips below fluid bubble point pressure. In the case where the fluid pressure dips below the fluid bubble point pressure, damage on the return side of the cycle, that is, the side where a high pressure is again encountered, is observed. The pressure excursion process for aircraft hydraulic systems appears to be initiated by simple accelerations of flow through a restricted passage from high to low pressure. Damage has been observed in the valve porting areas on servo valves, electrical depressurizing valves in pumps, pressure regulating valves, poppet relief valves, solenoid valves, check valves (ball or poppet) and in general wherever a large pressure drop exists across a short seating region, that is, for example, the seating region where a valve seats in the pump. The cavitation damaged area that is seen in valve porting areas on microscopic analysis has the following appearance: jagged, cinderlike, irregular, rough, undermined, peak-valley and cavities. The damage observed by microscopic analysis does not exhibit coloration or pitting such as would be found by corrosion, gouges, scratches, such as would be exhibited by machining, fatigue spalling such as would be observed by the sudden removal by large particles, particle erosion which would be exhibited by smooth and rounded edges or by wear wherein microscoring and metal transfer is observed. Thus, damage in a hydraulic system and in particular aircraft hydraulic systems which is subject to cavitation damage can be determined by comparing under microscopic examination damaged areas of valves with similar valves which are subject to the phenomenon of wear, fatigue spalling, corrosion, machining and particle erosion. In addition, valves undergoing damage by the process of cavitation can be compared with known specimen which have been subjected to induced cavitation damage. An example of this type of a comparison is a comparison of damaged metal tips in the vibrating probe with damaged valves from a hydraulic system. A comparison of this type can demonstrate damage in a hydraulic system since the vibrating probe gives a characteristic damage spectrum which is exhibited by valves in a hydraulic system.

In addition, apparatus have been invented which determine the leakage rate through valves in hydraulic systems and in particular aircraft hydraulic systems. These apparatus are referred to as leak detectors and can determine leakage rates in aircraft hydraulic systems. In addition, leakage rates can be continually monitored over a period of time. Thus, aircraft hydraulic systems which are subject to cavitation damage will exhibit increased leakage rates over a period of time as the geometry of the valve is altered through cavitation damage. It has been found that aircraft hydraulic systems operating utilizing functional fluid compositions of this invention when compared to aircraft hydraulic systems not using functional fluid compositions of this invention exhibit reduced leakage rates as a function of time based upon the above comparison. A type of leak detector for monitoring leakage rates is disclosed in application Ser. No. 630,667.

Utilizing the above methods a determination of whether or not an aircraft hydraulic system is subject to cavitation damage can be made. Any one or a combination of the test methods illustrated above can be utilized. The reduction in cavitation damage utilizing functional fluid compositions of this invention, in addition, can be determined utilizing the above test methods. Thus, it has been found that cavitation damage in an aircraft hydraulic system can be determined and in addition the reduction in cavitation damage utilizing functional fluid compositions of this invention can be determined. It has been found that a tremendous reduction in cavitation

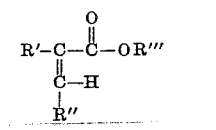
damage is observed when functional fluid compositions of this invention are compared to functional fluid compositions not having incorporated therein additive amounts of water when used in hydraulic systems subject to cavitation damage. Therefore as a result of the excellent control of damage utilizing the compositions of this invention, hydraulic systems and in particular aircraft hydraulic systems can have cavitation damage inhibited and controlled continually from the time of introduction of the functional fluid compositions of this invention into a hydraulic system. Thus, included within this invention is a process for continually controlling cavitation damage in a hydraulic system which is subject to cavitation damage when operated using a hydraulic fluid comprising a major amount of a amide of an acid of phosphorus as a base stock having incorporated therein a damage-inhibiting amount of additive water.

As a result of the excellent inhibition and control of damage utilizing the functional fluid compositions within the scope of this invention, improved hydraulic pressure devices can be prepared in accordance with this invention which comprise in combination a fluid chamber and an actuating fluid composition in said chamber, said fluid comprising a major amount of one or more of the base stocks hereinbefore described and a damage-inhibiting amount of water. In such a system, the parts which are so lubricated include the frictional surfaces of the source of power, namely the pump, valves, operating pistons and cylinders, fluid motors, and in some cases, for machine tools, the ways, tables and slides. The hydraulic system may be of either the constant volume or the variable-volume type of system.

The pumps may be of various types, including centrifugal pumps, jet pumps, turbine vane, liquid piston gas compressors, piston-type pump, more particularly the variable-stroke piston pump, the variable-discharge or variable-displacement piston pump, radial-piston pump, axial-piston pump, in which a pivoted cylinder block is adjusted at various angles with the piston assembly, for example, the Vickers Axial-Piston Pump, or in which the mechanism which drives the pistons is set at an angle adjustable with the cylinder block; gear-type pump, which may be spur, helical or herringbone gears, variations of the internal gears, or a screw pump; or vane pumps. The valves may be stop valves, reversing valves, pilot valves, throttling valves, sequence valves, relief valves, servo valves, nonreturn valves, poppet valves or unloading valves. Fluid motors are usually constant or variable-discharge piston pumps caused to rotate by the pressure of the hydraulic fluid of the system with the power supplied by the pump power source. Such a hydraulic motor may be used in connection with a variable-discharge pump to form a variable-speed transmission. It is, therefore, especially important that the frictional parts of the fluid system which are lubricated by the functional fluid be protected from damage. Thus, damage brings about seizure of frictional parts, excessive wear and premature replacement of parts.

The fluid compositions of this invention when utilized as a functional fluid can also contain dyes, pour point depressants, metal deactivator, acid scavengers, antioxidants, defoamers in concentration sufficient to impart antifoam properties, such as from about 10 to about 100 parts per million, viscosity index improvers such as polyalkylacrylates, polyalkylmethacrylates, polyurethanes, polyalkylene oxides and polyesters, lubricity agents and the like.

The preferred polymeric viscosity index improvers which may be employed in the compositions of this invention are the polymers of alkyl esters of alpha-beta unsaturated monocarboxylic acids having the formula



wherein R′ and R″ are each individually hydrogen or a C_1 to C_{10} alkyl group, and R‴ is a C_1 to C_{12} alkyl group. Illustration of the alkyl groups represented by *R′R″ and R‴ within their definitions as given above are for example methyl, ethyl, propyl, butyl, t-butyl isopropyl,* 2-ethylhexyl, hexyl, decyl, undecyl, dodecyl and the like. These polymers include, for example, poly(butymethacrylates), poly(hexylmethacylates), poly(octylacrylates), poly(dodecylacrylates) and polymers wherein the ester is a mixture of compounds obtained by esterifying the α-β unsaturated monocarboxylic acid with a mixture of monoalcohols containing from 1 to 12 carbon atoms.

The polyalkylmethacrylates and acrylates suitable for the purpose of this invention are in general those resulting from the polymerization of alkymethacrylates or alkylacrylates in which the alkyl groups have from four to 12 carbon atoms. The alkyl groups may be mixtures such as derived from a mixture of alcohols in which case there may be included some alkyl groups having as low as two carbons atoms and as high as about 18 carbon atoms. The number of carbon atoms in the alkyl groups should preferably be such that the polymer is compatible with the particular fluid used. Usually it will be satisfactory for the alkyl group of the methacrylate polymer to be from about four to 10 carbon atoms. The alkyl group may be branched chain or isoalkyl, but it is preferably normal alkyl. The molecular weight of the polymerized alkylmethacrylate can be from 5,000 to about 40,000. The total amount of viscosity index improver employed in the compositions of the instant invention can range from about two to about 20 parts per 100 parts of the total composition.

It has also been found that small amounts added to the base stocks as aforedescribed alone or as a fluid composition containing other base stocks in varying proportions gives improved resistance to metai erosion. The other base stocks hereinafter described also show the improvement when employed as the sole base fluid of a hydraulic fluid which contains the damage inhibiting amount of water. Such other base stocks are, for example, the esters of an acid of phosphorous e.g. phosphates, phosphonates, phosphinates, etc., amides of an acid of phosphorus orthosilicates, organopolysiloxanes, polyesters, liquid polyphenyl ethers and thioethers, chlorinated biphenyls and the like. Typical examples of these phosphate esters are for example, dibutylphenyl phosphate, triphenyl phosphate, tricresyl phosphate, tributyl phosphate, tri-2-ethylhexyl phosphate, trioctyl phosphate, and mixtures of the above phosphates such as mixtures of tributyl phosphate and tricresyl phosphate, mixtures of isooctyl diphenyl phosphate and 2-ethylhexyl diphenyl phosphate, and mixtures of trialkyl phosphates and tricresyl phosphates and the like. The particularly preferred phosphate esters are those which remain liquid at temperatures of about 30° C.

Typical examples of the amides of an acid of phosphorus, that is, mono- , di- and triamides of an acid of phosphorus, are phenyl-methyl-N,N-dimethylphosphoroamidate, phenyl-methyl-N-methyl-N-n-butylphosphoramidate, mixtures of phenyl-m-cresyl-N-methyl-N-butylphosphoroamidate and phenyl-p-cresyl-N,N-dimethylphosphoroamidate, mixtures of m-cresyl-p-cresyl-N-methyl-N-propylphosphoramidate, di-m-cresyl-N,N-dimethyl-phosphosoamidate, di-p-cresyl-N,N-dimethylphosphoroamidate, di-m-bromophenyl-N-methyl-N-n-butylphosphoroamidate, di-m-chlorophenyl-N-methyl-N-n-butylphosphoroamidate, di-alpha,-alpha, alpha-trifluoro-m-cresyl-N-methyl-N-n-butylphosphoro-amidate, di-p-bromophenyl-N-methyl -N-n-isoamylphosphoroamidate, di-p-chlorophenyl-N-methyl-N-n-isoamylphosphoroamidate, p-chlorophenyl-m-bromophenyl-N-methyl-N-n-isoamylphosphoroamidate, phenyl-N-methyl-N′-methyl-N′-butylphosphorodiamidate, phenyl-N,N-di-n-butyl-N′,N′-di-n-butylphosphorodimidate, phenyl-N,N-dimethyl-N′,N′-dimethylphosphoroamidate, m-chlorophenyl-N-methyl-N-N-butyl-N′-methyl-N-n-butylphosphorodiamidate, m-bromophenyl-N-methyl-N-n-butyl-N-methyl-N′-n-butylN′-methyl-N′-n-butylphosphorodiamidate, p-chlorophenyl-N-methyl-N-isobutyl-N′-methyl-N′-isoamylphosphorodiamidate, p-bromophenyl-N-methyl-N-

isobutyl-N'-methyl-N'-isoamylphosphorodiamidate, N-methyl-N2butyl-N'-methyl-N'-butyl-N''-methyl-N''-butylphosphorotriamidate, N-methyl-N-butyl-N',N''-tetramethyl-phosphorotriamidate, N-di-n-propyl-N',N''-tetramethylphosphor-tramidate and N,N'-di-n-propyl-N''-dimethylphosphorotriami-date.

Typical example of orthosilicates useful as base stocks include the tetraalkyl orthosilicates such as tetra(ocytl)orthosilicates, tetra(2-ethylhexyl orthosilicates and the tetra(isooctyl)orthosilicates and those in which the isooctyl radicals are obtained from isooctyl alcohol which is derived from the oxo process, and the (trialkoxysilico)trialkyl orthosilicates, otherwise referred to as hexa(alkoxy) disiloxanes, such as hexa(2-ethylbutoxy) and hexa(2-ethylhexoxy)disiloxane.

The polyphenyl ethers contemplated are for example bis(m-phenoxyphenyl) ether, m-bis(m-phenoxyphenoxy)benzene, m-bis(p-phenoxyphenoxy)benzene, o-bis(o-phenoxyphenoxy)benzene, bis[m-(m-phenoxyphenoxy)phenyl]ether, bis]p-(p-phenoxyphenoxy)-phenyl]ether, m-[(m-phenoxyphenoxy)(o-phenoxyphenoxy)]ether, m-bis[m- (m-phenoxyphenoxy)phenoxy]benzene, p-bis[p-(m-phenoxyphenoxy)phenoxy]benzene, m-bis[-p-phenoxyphenoxy)phenoxy]benzene and mixtures thereof with other polyphenyl ethers.

Examples of polyphenyl thioethers and mixed polyphenyl ethers and thioethers are 2-phenylmercapto-4'-**phenoxydiphenyl sulfide**, 2-phenoxy-3'-**phenylmercaptodiphenyl sulfide**, **o-bis-(phenylmercapto)benzene**, **phenylmercaptobiphenyl**, **bis(phenylmercapto)biphenyl**, **m-(m-chlorophenylmercapto)-m-phenylmercaptobenzene**, **phenylmercapto(phenoxy)biphenyl**, **m-chlorodiphenyl sulfide**, **m-bis(m-phenylmercaptophenyl-mercapto)benzene**, 1,2,3-tris(phenylmercapto)benzene; 1-phenylmercapto-2,3-bis(phenoxy)-benzene, and the like.

The halogenated biphenyl functional fluid base stocks which can be employed in minor amounts in the composition of this invention are those having from 20 to 61 percent by weight combined chlorine. Typical examples of halogenated biphenyl compounds are those which contain chlorine or bromine or combinations thereof in amounts corresponding to mono- , di- , tri- , tetra- , penta- and hexahalobiphenyl. Typical of such biphenyl compounds are the chlorinated biphenyls commercially available as products containing 32 percent, 42 percent, 48 percent, 54 percent and 60 percent by weight of combined chlorine. The expression halogenated biphenyl containing a stated percentage of combined halogen is used herein as including the directly halogenated products, halogenated products containing more than one specie of halogen in the same molecule and blends of one or more of such halogenated products whereby the halogen content is broadly within the range of about 30 percent to 60 percent, preferably within the range of about 30 percent to 42 percent by weight.

The base stocks of this invention can also contain other fluids which include in addition to the functional fluids described above fluids derived from coal products, and synthetic oils, e.g., alkylene polymers (such as polymers of propylene, butylene, etc., and mixtures thereof), alkylene oxide-type polymers (e.g., propylene oxide polymers) and derivatives, including alkylene oxide polymers prepared by polymerizing the alkylene oxide in the presence of water or alcohols, e.g., ethyl alcohol, alkyl benzenes, (e.g., monoalkylbenzene such as dodecyl benzene, tetradecylbenzene, etc.), and dialkylbenzenes (e.g., n-nonyl-2-ethyl hexylbenzene); polyphenyls (e.g., biphenyls and terphenyls), hydrocarbon oils including mineral oils derived from petroleum sources and synthetic hydrocarbon oils, examples of which are mineral oils having a wide range of viscosities and volatilities such as naphthenic base, paraffinic base and mixed base mineral oils; synthetic hydrocarbon oils such as those derived from oligomerization of olefins such as polybutenes and oils derived from high-alpha-olefins of from eight to 20 carbon atoms by acid catalyzed dimerization and by oligomerization using trialuminum alkyls as catalysts; halogenated benzene, halogenated lower alkylbenzene and monohalogenated diphenyl ethers.

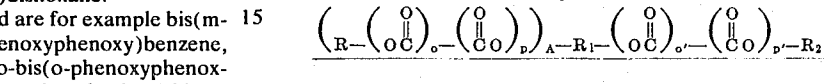
While this invention has been described with respect to various specific examples and embodiments, it is to be understood that the invention is not limited thereto and that it can be variously practiced within the scope of the following claims.

What is claimed is:

1. A method for controlling cavitation damage to mechanical members in a hydraulic system which comprises introducing and employing as the hydraulic fluid in said system a composition comprising

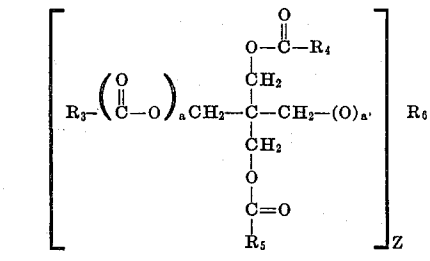
A. a major amount of at least 60 percent by weight of a synthetic ester fluid selected from the group represented by the formulas

1.



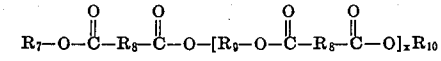
o o'p and *p'* each are whole numbers having the value of 0 or 1 provided that the sum of *o* +*p* and *o'*+*p'*is 1; *A* is a whole number having the value of 1 or 2; *R* and R_2 are each independently selected from the group consisting of alkyl and alkoxylalkyl groups containing from two to 18 carbon atoms and R_1 is an alkylene group containing from 2 to 12 carbon atoms,

2.



wherein R_3, R_4 and R_5 are each alkyl groups containing from two to 18 carbon atoms, *a* and *a'*are whole numbers having a value of 0 or 1, *Z* is a whole number having a value of 1 to 4 and when *Z* is 1 *a'*is 0 and R_6 is an acyloxy group containing from three to 12 carbon atoms and when *Z* is 2 to 4 *a'*is 1 and R_6 is acyl containing from 3 to 12 carbon atoms,

3.



wherein R_7 and R_{10} are each an alkyl group containing from three to 10 carbon atoms R_8 and R_9 are each an alkylene group containing from two to 12 carbon atoms, *x* is a whole number having a value of 1 to about 80 or more and

B. a damage inhibiting amount of water in the range of from 0.2 to 5 volume percent.

2. The method of claim **1** wherein *R* and R_2 are each independently selected from the group consisting of alkyl groups containing from two to 18 carbon atoms.

3. The method of claim **1** wherein the compositions also contain up to 20 percent by weight of a viscosity index improver.

4. The method of claim **3** wherein the viscosity index improver is a polyalkylacrylate, a polyalkylmethacrylate, a polyurethane, or a polyalkylene oxide.

5. The method of claim **1** wherein the synthetic ester fluid is (A) (1).

6. The method of claim **1** wherein the synthetic ester fluid is (A) (2).

7. The method of claim **1** wherein the synthetic ester fluid is (A) (3).

8. The method of claim **1** wherein the water is present within the range of from 0.30 to about 3 volume percent.